Microscopic Models of Precursor Film Dynamics[1]

Esteban Moro[2,3] and Douglas B. Abraham[2]

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[2]Theoretical Physics, University of Oxford

1 Keble Road, Oxford OX1 3NP, United Kingdom.

[3]To whom correspondence should be addressed.

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Abstract

We consider a model for the phenomenon of droplet spreading when there is a precursor film. The mechanism of growth involves diffusion of particles in a supernatant gas described as a monolayer located directly above the precursor film. Particles enter from the reservoir droplet and exit at the edge of the precursor where they fall to the substrate plane causing the precursor to grow. There is an analogous phenomenon of hole diffusion within the precursor film itself. The techniques we employ are Monte Carlo simulations and non-linear surface growth equations. We investigate the roughness of the outer edge of the precursor film as a potential characteristic of the model in question. Our approach is both numerical and analytic and allow us to treat both interaction between particles and the substrate (regarded as a continuum) and interparticle interactions. It is to be hoped that the roughness characteristics will be confirmed experimentally.

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1 Introduction

In 1989, a stimulating review article published in Nature by P. M. Ball [1] drew the attention of condensed matter theorists to the lack of a theory (even a formative one) to explain the highly interesting experimental work on spreading recently carried out in France [2]. The system in question is various pure silanols spreading across an extremely flat silicon wafer with oxidized surface. The thickness of the film is measured by ellipsometry. Purity is maintained by pumping dry nitrogen through the system. This does not cause any significant effect during an experiment; thus the mechanism of spreading does not involve evaporation into the spectator phase, followed by redeposition.

The experiments show that as the reservoir drop spreads over the plane substrate, it is preceded by a film about 10 Å thick which is extremely flat and which can be followed over large distances ($\simeq 10^7$ Å). The precursor film thickness is determined by ellipsometry showing that the edge of the precursor film spreads according to the universal law $\bar{h}(t) \propto t^{1/2}$.

Since then, a variety of theoretical models have been proposed to explain this behavior. In all of them, the spreading of the precursor film is due to unbalanced spreading forces caused by the attraction of the substrate. Apart from that, different growth laws are obtained depending on the model. In particular, the $t^{1/2}$ law has been reproduced in the molecular dynamics (MD) simulations involving Lennard-Jones molecules [3] or chainlike molecules [4]. In another approach, effective solid-on-solid models has been considered in an attempt to reduce the greater number of degrees of freedom [5]. Unfortunately, they give incorrect large-time behaviour of $\bar{h}(t)$. From the Monte Carlo simulations of these simplified models it is easy to realize the driving mechanism of the precursor film: the migration of matter from the precursor edge to the droplet reservoir. This migration takes place due to the diffusion of holes from the precursor to the reservoir and/or due to molecular evaporation from the reservoir into a dilute supernatant gas phase directly above

the precursor film and their diffusion to the precursor edge. In both cases, the mean time needed for the particle/hole to reach the edge/reservoir from the reservoir/edge is proportional to $h(t)$ so we can estimate $\partial_t h(t) \propto 1/h(t)$ recovering the law $h(t) \propto t^{1/2}$.

Although the mean displacement of the precursor film has been studied extensively during the last decade, no attention has been devoted to the shape of the precursor edge. Ellipsometry allows high (atomic) resolution normal to the substrate, but insufficient in the plane to analyze the shape of the precursor edge. However new microscopy techniques will allow to obtain information about the precursor edge. On the other hand, the knowledge of more properties of these phenomena will offer, from the theoretical point of view, the answer on the question about which model is suitable to reproduce the experimental behaviour. Our approach in this communication is to study one of these models and, in particular, the roughness of the precursor edge, a quantity we believe could be accessible from experiments. As we will see, the interface is a self-affine fractal, being characterized by universal power laws and exponents.

The outline of the paper is at follows: in section 2 we introduce the model and describe its main properties. Simulations for this model are presented in section 3, while a coarse-grained mesoscopic equation for the interface is presented in section 4. Finally we discuss our results in 5.

2   Microscopic model

As in Ref. [6] we consider a lattice gas model with fluid particles interacting with their nearest neighbors via the coupling constant J, which describes the cohesion between fluid particles and is closely related to the surface tension. We also assume the interaction between the fixed structureless substrate and the liquid particles to be of the attractive van der Waals form $V(z) = -A/z^3$, where z is the distance from the substrate and A is proportional to the Hamaker constant. In the original

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reference, the microscopic dynamics is that of a lattice gas in which we assume that the region above the substrate which is accessible to molecules is divided into a set of cells whose centers form a regular lattice, and with proper initial conditions. In our case, and for sake of feasibility, we consider only particles close to the substrate, i.e. only two vertical layers $z = 1, 2$ which is the simplest configuration to take into account both the precursor film and the supernatant gas. Within this approximation the droplet reservoir is approximated by a boundary condition by which molecules are fed in the lattice gas at a constant rate. We focus here on systems with planar geometry, i.e., on systems in which the film spreads effectively only along one spatial coordinate, e.g. y. Thus simulations are performed in 3D rectangular box $(x, y, z) \in [1, L_x] \times [1, L_y] \times [1, 2]$ (see Fig. 1). In each cell of the lattice, denoted by $i = (x, y, z)$ we define the occupation number $\eta_i(t)$ to be one or zero depending on whether the cell is occupied or not by a molecule. A molecule is said to be in the supernatant gas if its vertical position over the substrate is $z = 2$, while the precursor film is made of particles with $z = 1$. The droplet reservoir boundary condition is set along the line $y = 1$, and throughout this communication we will fix this boundary condition to be that by which $\eta_i(t) = 1$ for $y = 1$.

A particle can perform a jump to a unoccupied neighbour place in the lattice with a hopping rate given by

$$r(i \to f) = \nu e^{-\beta \Delta \mathcal{H}_{i \to f}} \tag{1}$$

where $\Delta \mathcal{H}_{i \to f}$. is the energy difference between the final and initial, ν is the activation rate in the supernatant/precursor film and $\beta = 1/k_B T$. We will suppose that this energy difference is given by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{l,l} + \mathcal{H}_{l,s} \tag{2}$$

where

$$\mathcal{H}_{l,l} = -\frac{J}{2} \sum_{\langle i,j \rangle} \eta_i \eta_j \tag{3}$$

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is the interaction between particles, with $\langle i, j \rangle$ meaning the sum over nearest neighbours, and

$$\mathcal{H}_{l,s} = -A \sum_i \eta_i \qquad (4)$$

is the interaction with the substrate. The sum in (4) is performed over all the positions in the lattice with $z = 1$. Because we are only considering the case $z = 1, 2$ the Hamaker constant in (4) has been rescaled to be A when $z = 1$ and zero if $z = 2$.

To reproduce the experimental results we have used time continuous Monte Carlo simulations in order to present the results in real time. We normalize the activation rate to be $\nu = 1$, and the size of the lattice was chosen $L_y = 4096$ with L_x ranging from $L_x = 32$ to $L_x = 256$. Temperature is maintained below the 3D and 2D Ising model critical values. Thus, it is small enough to maintain a low vapor pressure both in 3D and 2D, that is, particles tend to be in the condensed/liquid phase. Also we have chosen A to be large enough to prevent evaporation of single particles from the substrate. Within these restrictions, several mechanism are unfavorable energetically, like evaporation from the precursor film to the supernatant gas or detaching of particles from the precursor edge and a subsequent free diffusion over the substrate.

During the spreading process, several mechanisms are responsible for the precursor edge growth: (i) first, fluctuations in the precursor film allow hole formation. These holes perform random motions and part of them eventually move towards the reservoir where they die. (ii) second, particles from the reservoir will diffuse in the supernatant gas over the precursor film until they find a hole or the precursor edge, causing precursor film growth. (iii) particles can be detached from the precursor edge and then move diffusively over the substrate and, eventually, some of them come back to the edge. As already noted, J is chosen large enough to prevent evaporation in 2D, so these later events are suppressed energetically. Within these considerations, the numerical values used throughout this communication are $A/k_B T = 10$ and $J/k_B T = 1$, so that 3D evaporation is almost suppressed, but a small amount of 2D evaporation over the substrate is allowed.

3   Simulation results

In this section we present the results for the model. Firstly we have to identify the interface, i.e. the precursor edge. This is not obvious, since the interface has holes and overhangs. Nevertheless, we have used the cluster method in which the interface $h(x,t)$ is given by the maximum value for a fixed value of x of the length y for the particles that belong to the main cluster. A particle is in the cluster if it is connected to the droplet reservoir or/and a nearest neighbor which is in the cluster. With this definition, we compute the mean height

$$\bar{h}(t) = \sum_{x=1}^{L_x} \langle h(x,t) \rangle, \tag{5}$$

where $\langle \cdots \rangle$ stands for the average over different realizations of the Monte Carlo simulation, and the interface roughness

$$w^2 = \sum_{x=1}^{L_x} \langle (h(x,t) - \bar{h}(t))^2 \rangle. \tag{6}$$

Results presented in Fig. 2 show that we indeed recover the universal law $\bar{h}(t) \propto t^{1/2}$, but only for large values of t. More interesting results are obtained for the roughness, which grows in time like

$$w^2(t) \propto t^{2\beta}, \tag{7}$$

before it saturates to a value, $w_{sat}^2(L_x)$ that depends on the system size like $w_{sat}^2(L_x) \propto L_x^{2\alpha}$. This behaviour reflects that the interface is *self-affine* [7] and thus, its main properties can be described in terms of the α and β exponents which in turn define the universality class of the growth phenomena. The results presented in this communication allow us to determine the exponent β, and some indications about the possible value of α, but not a final answer about the universality properties of the interface. Regarding the exponent β in Fig. 2 we see that its value from numerical simulations is given by $\beta = 0.095 \pm 0.006$. Although the value is small it is definitely non-zero, thus ruling out a logarithmic dependence.

To obtain the α exponent we will use the interface structure factor,

$$S(q_x) = \langle \hat{h}(q_x,t)\hat{h}(-q_x,t) \rangle, \tag{8}$$

where $\hat{h}(q_x, t)$ is the Fourier transform of $h(x, t)$. In the self-similar scenario for the interface, and once the system has reached the asymptotic regime, the structure factor scales as

$$S(q_x) \simeq q_x^{-d-2\alpha}, \tag{9}$$

which allow us to obtain numerically the value of α. In Fig. 3 we plot the structure factor showing that the data is compatible with $d + 2\alpha \simeq 5/2$, that is $\alpha \simeq 1/3$.

We have checked that these results are independent of the parameters used in this section as long as the temperature is below the 2D bulk critical temperature, which in this case is estimated by the Ising model critical temperature $J/T \simeq 0.567$. Also, the exponents are consistent for different values of $32 < L_x < 256$. Nevertheless a different value of α and β can not be excluded for larger lateral sizes ($L_x > 256$, which would change the universality class (see the discussion below).

4 Mesoscopic interface model

In the case of a well defined interface one is tempted to describe its evolution by a stochastic differential equation

$$\frac{\partial h}{\partial t} = F(h, \nabla h, \nabla^2 h) + \eta \tag{10}$$

where η is the noise. This formulation in terms of stochastic differential equations has been a successful framework for the study of rough interface dynamics and has allowed to classified the different universality classes. Generally, in this models the interface growth is described by processes that take place over the interface, like adsorption, diffusion, desorption, etc., thus neglecting bulk dynamic processes. However, in the spreading model studied above the interface growth and shape is mainly due to both diffusion of particles in the bulk and over the interface. Despite these differences and whenever the creation of holes at the interface and the flux of incoming particles from the supernatant gas is small enough (i.e. when the bulk

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dynamics is slow enough compared to the interface dynamics), our hope is that we can still describe the interface by a equation like (10).

We now consider the form of the term $F(h, \nabla h, \nabla^2 h)$. Firstly, there is a conserved diffusion of matter over the interface. Thus the local changes in the interface height $h(x, t)$ are the result of the nonzero currents along the surface. Neglecting desorption, the total number of particles remains unchanged during the diffusion process, and then the current over the interface $j(x, t)$ must obey the continuum equation

$$\frac{\partial h(x, t)}{\partial t} = -\nabla \cdot j(x, t). \tag{11}$$

Assuming local behaviour, the current is given by the difference of a chemical potential $j(x, t) \propto -\nabla \mu(x, t)$. On the other hand, interface diffusion is the result of activation of atoms in the interface, a process that depends on the number of neighbors the atom has. Thus, we could approximate the chemical potential to be inversely proportional to curvature, and so $\mu(x, t) \propto -\nabla^2 h(x, t)$. Taken into account the randomness present in the activated diffusion over the surface we end up with the following equation

$$\frac{\partial h(x, t)}{\partial t} = -\kappa \nabla^4 h(x, t) + \eta_d(x, t) \tag{12}$$

where $\eta_d(x, t)$ is a diffusive conservative noise:

$$\langle \eta_d(x, t) \rangle = 0, \quad \langle \eta_d(x, t) \eta_d(x', t') = -\nabla^2 \delta(x - x') \delta(t - t') \rangle \tag{13}$$

Equation (12) is the linear approximation for conservative diffusion over a general interface. In our case, the interface growth is not symmetric under the transformation $h \rightarrow -h$, so we expect non-linear terms to be important. The simplest non-trivial term is that given by the conservative KPZ-type non-linearity

$$\frac{\partial h(x, t)}{\partial t} = -\kappa \nabla^4 h(x, t) + \frac{\lambda}{2} \nabla^2 (\nabla h)^2 + \eta_d(x, t) \tag{14}$$

This equation was introduced and studied by Sun *et al.* [8] to study the dynamics of a growing interface in which a conservation law is present. Nevertheless, the surface

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grows because of deposition of new material from the supernatant gas or because of migrations of holes in the precursor film of holes from the edge to the droplet reservoir. This process is non-conservative and depends on the local curvature, because is an activated process that depends on the number of neighbors a molecule has. Up to first order we could assume that locally, the growth rate for this desorption/adsorption process is given by a $\nu\nabla^2 h$ term, and possibly by a non-linear KPZ-like nonlinearity and a noise source. If both $\nu\nabla^2 h$ and $\kappa\nabla^4$ terms are present in the dynamics, the $\kappa\nabla^4$ term determines the scaling behavior for $L_x \ll L_x^* = (\kappa/\nu)^{1/2}$ [7]. However for $L_x \gg L_x^*$, the $\nu\nabla^2 h$ term controls the scaling behaviour. Thus, we expect that in this large-scale regime the interface will be described by

$$\frac{\partial h(x,t)}{\partial t} = \nu\nabla^2 h(x,t) + \frac{\lambda}{2}(\nabla h)^2 + \eta(x,t) \tag{15}$$

where $\eta(x,t)$ is the usual non-conservative white noise. This equation was introduced by Kardar *et al.* to study the interface when lateral growth is included [9]. Exponents for both eqs. (14) and (15) are known in one dimension. In the case of conservative diffusion we obtain $\alpha = 1/3$ and $\beta = 1/11$, while for non-conservative growth, $\alpha = 1/2$ while $\beta = 1/3$. Comparing these theoretical values with our simulations we obtain a rather accurate description of the interface by the Eq. (14) when the lateral size $L_x < 256$. This result does not exclude the possibility that Eq. (15) describes the system at large scales, but the crossover, L_x^* between the regimes described by (14) and (15) could be large enough to be reached in our simulations or even in the experiments.

5   Discussion and conclusion

In summary, we have studied the interface dynamics of a microscopic model for precursor film spreading. In the simulations we reproduce the observed universal $t^{1/2}$ law for the precursor edge growth. Moreover, we have found that the interface is self-similar and that its properties can be described in terms of some exponents α

and β. From this considerations we have proposed a effective conservative stochastic differential equation for the interface dynamics which is able to reproduced the behaviour found in the simulations. Nevertheless, we argue that as well as the system size is increased, the properties of the interface could change to a non-conservative regime described by the KPZ equation. We hope that this work will stimulate some experiments and simulations to verify our predictions about the way the precursor film spreads over the substrate.

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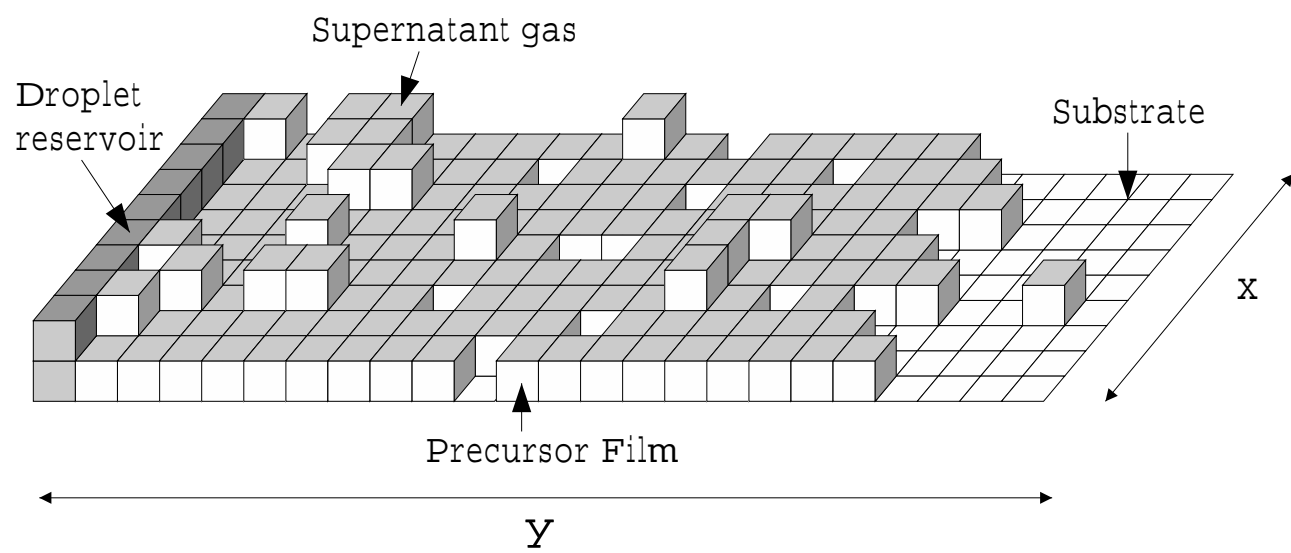
Figure Captions

Figure 1. Cartoon of the microscopic model.

Figure 2. Time dependence of $\bar{h}$ (solid line). Simulations are for $L_x = 64$. The dashed line is the law $t^{1/2}$.

Figure 3. Time dependence of the roughness $w^2(t)$. Simulations are for $L_x = 64$. The dashed line is a power law fit to $t^{0.095\pm0.006}$.

Figure 4. Structure factor of the precursor edge (solid line). Simulations are for $L_x = 64$. The dashed line is the power law $q_x^{-5/2}$.
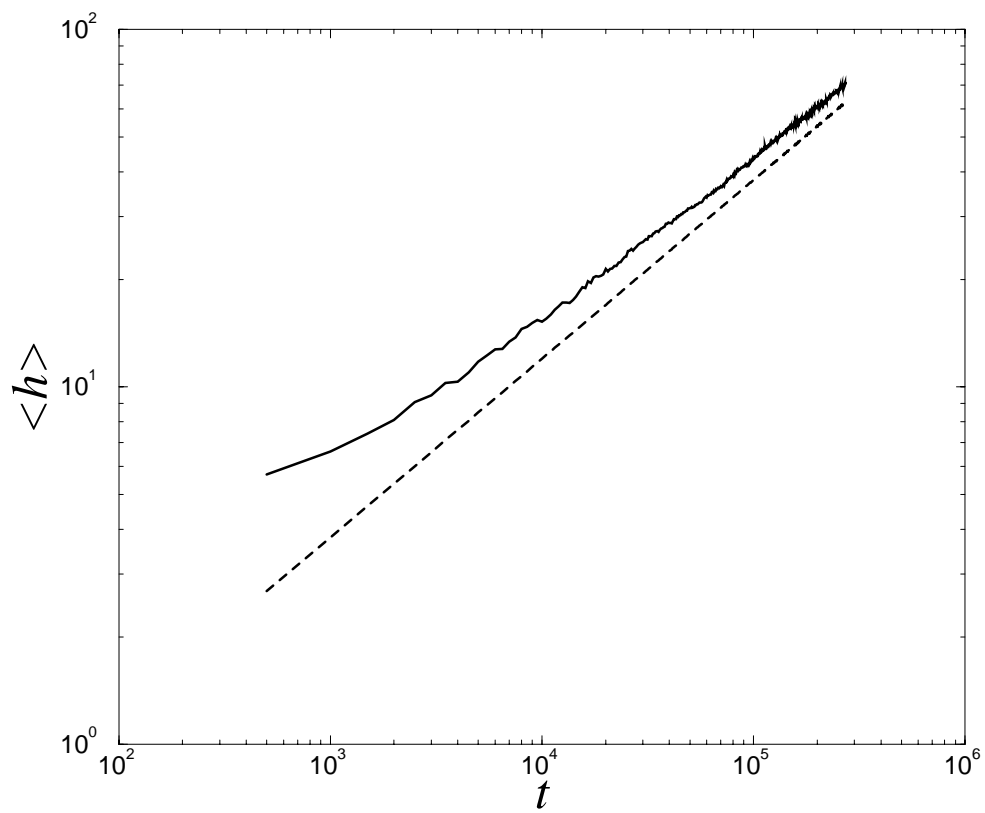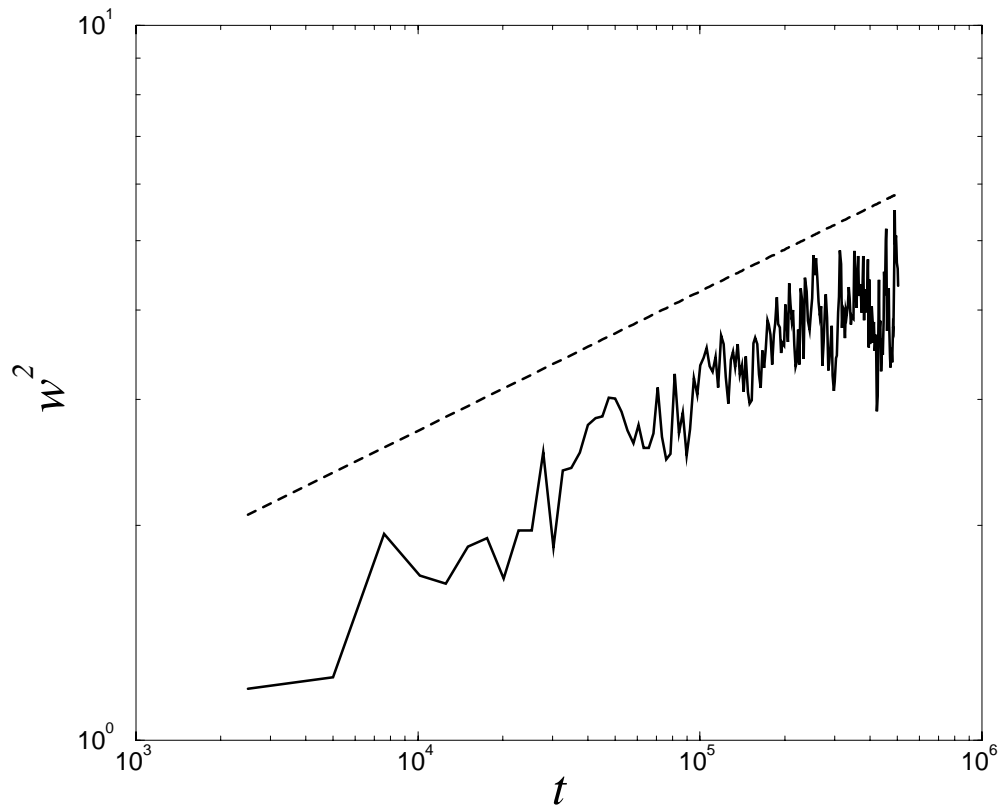
Droplet reservoir

Supernatant gas
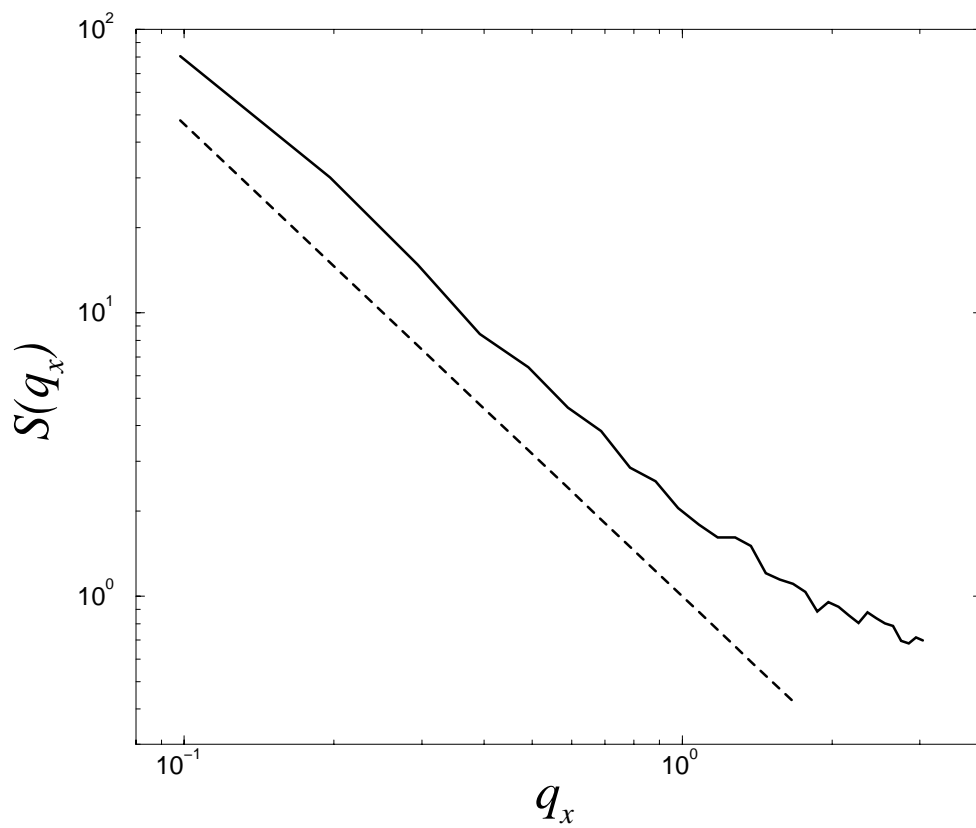
Substrate

Precursor Film

x

y

Figure 1:

14

Figure 2:

15

Figure 3:

Figure 4: